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XXI. *Researches on Turacin, an Animal Pigment containing Copper.* By A. H. CHURCH, M.A. Oxon., Professor of Chemistry in the Royal Agricultural College, Cirencester. Communicated by Dr. W. A. MILLER, Treas. and V.P.R.S.

Received May 4,—Read May 27, 1869.

Origin of the present Inquiry.—The stability of the colours which the feathers of birds display has been repeatedly proved. These colours are due either to what we may call the optical character of the surfaces of the web, or to the presence in it of definite colouring-matters. These pigments may be opaque like enamel, or translucent and permeating the substance of the barbs; they have been as yet but very imperfectly studied. In a few instances only have they been actually separated from the structures containing them, while in no case have they been completely examined from a chemical point of view. So far as I can learn, we have no exact information as to the amount and the deportment, chemical constitution and reactions of those substances which M. BOGDANOW*, some twelve years ago, succeeded in extracting from the feathers of many birds, and notably from the red feathers of *Calurus auriceps* and *Catinga cærulea*. Before giving an outline of my own experiments in this direction, I will mention the particular circumstances which led to the prosecution of the present research.

A few years ago Mr. W. B. TEGETMEIER pointed out to me a singular property of the red feathers of the bird called the Touracou, or Plantain-eater. These feathers yield up a part of their colouring-matter to pure water, a beautiful rose-coloured solution being thus obtained. Mr. TEGETMEIER's attention had been drawn to this fact, and he at once perceived that it was worthy of fuller investigation than it had already received. On further inquiry, I find that Mr. WARD of Wigmore Street had noticed the evanescence and solubility of the red tint in question many years ago, and that other observers, within the last few years, have even succeeded in staining pieces of paper with the red solution which these feathers yield. In order that it may be seen what was the position of the inquiry when I commenced in 1866 my experiments on this subject, I may cite the authority of some private letters which have been placed at my disposal through the courtesy of Mr. HUGH OWEN. These letters were written by Dr. BENJAMIN HINDE, principal Medical Officer on the Military Staff at Bathurst, on the Gambia. In one of his letters, dated May 1865, Dr. HINDE enclosed a piece of paper stained with the red pigment of 1 inch of a feather of the violet Plantain-eater, *Musophaga violacea*. He says that the moment soap touches the feathers the colour runs, but that it is difficult of extraction with pure water. But he adds, "the birds I sent home washed themselves

* Comp. Rend. xlv. p. 688; xlv. p. 780.

nearly white in the water left for them to drink!" In a subsequent letter Dr. HINDE gives some details concerning the different species of Plantain-eaters, and says, with reference to the feathers he had previously sent to England, "all the feathers sent were from the same bird and grew in this house." This fact negatives any idea of an artificial dye being present in the feathers, and is further referred to in the following memoranda by Mr. HUGH OWEN:—"A pair of violet Plantain-eaters from the Gambia were sent over to a friend in Ireland by Dr. HINDE. The birds arrived in excellent condition, and were speedily provided with ample space and all appliances for cleanliness. For a while this splendid plumage, the deep crimson patch on the dark violet of the wing, excited continual admiration. After a day or two the crimson faded; in a few more the colour changed to a pale and dirty grey. The disappointed owner wrote an account of this change to Bathurst, concluding, of course, that the natives had imposed on Dr. HINDE by selling him a pair of painted birds: this, however, was impossible; there was no mistaking the peculiar and shield-shaped bill or the legs of the Musophaga. Whatever change had taken place, the birds were genuine Touracous. Without delay another bird was procured, so young as to be only partly fledged, the wings only in the pin-feathers. As soon as these were sufficiently grown, the experiment was repeated, and the colour found to be inconstant and capable of extraction." The data already given, and many others with which I have been subsequently furnished, incontestably prove the normal presence, in some of the feathers of the Plantain-eater, of a red pigment soluble in water, and still more readily dissolved by soap. I may now give my own results as to the preparation and physical and chemical properties of this new red animal pigment.

Occurrence of Turacin.—The birds from which I have extracted this colouring-matter generally go under the designation of Plantain-eaters, from their favourite food. It would appear that the native name for them is represented by the word Touraco; while the Dutch speak of one of the species as the Cape Lowry. These birds are entirely African. They belong to the Order Scansores and the Family Musophagidæ; they are closely related to the Cuculidæ or Cuckoos. There are three genera of Touracos—*Musophaga*, *Corythaix*, and *Schizorhis*—altogether including eighteen species. The red pigment occurs in twelve only of these birds, namely, in both the known species of *Musophaga* and in ten out of the eleven species of *Corythaix*. The eleventh species of *Corythaix*, in which it does not occur, is the Giant Touracou, which diverges in many other particulars from its brethren. The following is a list of the species from which I have actually obtained the pigment; in the others, named above, I have merely recognized its presence by optical means:—

Musophaga violacea.

Corythaix (Turacus) porphyreolopha.

— *erythrolopha.*

— *albocristata.*

The plumage of these birds does not present any great general brilliancy. The red pigment occurs in the primary and secondary pinion-feathers, from twelve to fifteen of

which have either a crimson blotch upon them, or are almost wholly coloured. I propose the name Turacin for the red pigment which the Touracou (*Turacus*) contains. In order to extract this pigment the plan finally adopted was as follows:—

Isolation of Turacin.—The barbs constituting the red part of the web are stripped from the shaft of the feathers, placed in a beaker, and washed with ether and then with alcohol. This treatment removes the grease and adhering dirt very effectually. When the red barbs thus washed have been dried between folds of filter-paper, they are placed in a cold very dilute solution of pure caustic soda, a solution containing one part of soda in a thousand of distilled water being quite strong enough. Ammonia, potash, or the carbonated alkalies may be used in lieu of caustic soda. The mass is stirred at intervals for fifteen minutes, or thereabouts; the crimson solution is poured off and pure water added; by successive treatment of the barbs with fresh portions of dilute alkali and pure water, the whole of the crimson pigment is obtained in solution, the residual barbs becoming white or pinky grey. All the coloured liquors having been filtered and mixed, they are poured in a slender stream, with constant stirring, into dilute hydrochloric acid, made by mixing one part of the pure commercial acid with four parts of water. When the red precipitate of the pigment thus coagulated and rendered insoluble has settled, the supernatant liquid is decanted off and the red matter thrown upon a wetted filter and washed with water. (A still better plan is to employ a decanting siphon filter for the separation and washing of the precipitate.) The liquid comes through quite colourless, until there is no longer a trace of acid left in the pigment on the filter. When this occurs, the residue is washed with water containing a few drops of acetic acid to the pint, and then syringed out of the filter into an evaporating-basin and dried at a gentle heat. The dry pigment is next to be washed with a mixture of alcohol and ether, and once more dried. It is now perfectly pure and yet unchanged, so far as I have examined it.

Properties of Turacin.—Prepared as above described, turacin occurs in scales which have a deep violet-purple colour by reflected light, and showing a crimson tint when seen in small fragments by transmitted light. Its powder is of a dull crimson tint. It has not been obtained in a crystalline form. It is very slightly soluble in pure water, giving a pale rose-pink solution. The presence of acids and salts renders water incapable of dissolving it. It is not soluble in pure alcohol or ether. In alkaline liquids it immediately dissolves, forming solutions which show a bluer tint than the original pigment. In fact turacin is a very delicate test for the alkalies. For example, perfectly pure barium hydrate in solution does not dissolve turacin; but let a minute trace of soda exist, as it often does, in the baryta-solution, and then the liquid will become readily tinted if shaken up with a fragment of turacin. Very strong solutions of the caustic alkalies dissolve the pigment, but at the same time it suffers a partial decomposition, evidenced by an odour resembling that of certain bases of the pyridine series, which it then evolves. Fuming nitric acid dissolves it with a deep brown tint, destroying it; in oil of vitriol it is soluble, but in all probability with partial alteration. Turacin seems to have slightly acid properties; though it dissolves very freely in carbonated alkalies,

caustic alkalies are still more effective. Turacin by long exposure to air and moisture, or by continued ebullition with water or alkaline liquids, acquires a colour closely resembling that of chlorophyll.

Spectrum of Turacin.—If a piece of the red web of a Touracou's feather be examined with a prism, two black bands will be at once perceived about the lines D and E of the solar spectrum (fig. 1). These bands correspond to some extent with those of STOKES's red cruorin, but it will be seen (fig. 2) that they are not identical. When an alkaline solution of turacin is similarly examined, the bands (fig. 3) are shifted further from D,

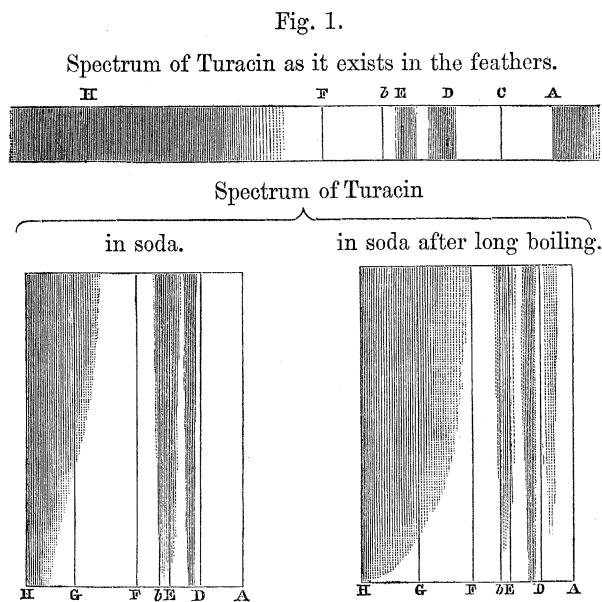
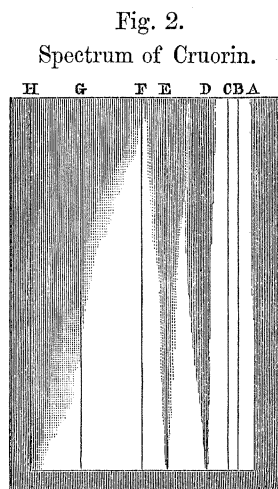


Fig. 3.

Fig. 4.



while the blue region of the spectrum is less shaded than it is with the original red of the feather, or with coagulated turacin precipitated by an acid. When the alkaline solution of turacin is dilute, the band near E is very weak; but when a strong solution is employed, both bands became equally intense, and finally almost coalesce, nearly obliterating the space in the green between them. No results have attended my attempts to produce in turacin, by ferrous or stannous salts, a reduction similar to that obtained in red cruorin by the same means. Coagulated turacin in water, and more particularly the web of the red feathers, present by transmitted light very nearly the appearance of diluted arterial blood to the eye.

The change in the colour of turacin produced by exposure to air and moisture may be traced in the spectrum of the altered substance (fig. 4). The specimen examined had been prepared by long boiling of a soda-solution of the original pigment, but it probably contained some unaltered turacin. In this modified spectrum a third black band has made its appearance in the orange, between D and C.

Composition of turacin.—The volatile constituents of turacin are carbon, hydrogen,

nitrogen, and oxygen, in what proportions I shall presently state. It contains no sulphur. The ash or non-volatile constituents of the new pigment have also been submitted to a careful examination.

Turacin may be dried at 100° without change; but at a considerably higher temperature its surface-colour alters, becoming bluish and then a dull green. Afterwards it shows some symptoms of fusion, giving off a violet vapour resembling that of iodine; it finally burns away, leaving a greyish-black ash.

The close resemblance of turacin to cruorin induced me to test at once, in the ash of the new colouring-matter, for iron, the characteristic metallic constituent of the pigment of the blood, and of its derivatives. The ash of turacin was dissolved in nitric acid, excess of sodic acetate added, and then potassic ferrocyanide. Much to my surprise, instead of the deep blue *ferric* ferrocyanide, a copious purple-brown precipitate of *cupric* ferrocyanide made its appearance. Not only was copper present, but there was so much of it that it could be detected by its spectrum when the ash of a few red barbs of the original feathers was moistened with strong hydrochloric acid and exposed on a platinum-wire to the flame of a Bunsen burner.

This detection of copper in the colouring-matter was so extraordinary that it became necessary to sift the matter thoroughly. The idea that a preservative solution containing copper had been used in dressing the skins of the birds suggested itself; but this notion was soon proved untenable; for there is no copper in any part of the skin save in the red feathers, and in these feathers themselves the presence of copper is strictly confined to the red barbs. Even barbs that are partly red and partly black contain no copper in their black parts, and abundance in those which are red. Moreover, as acids do not wash out the copper from the feathers, and the most severe chemical treatment, short of actual destruction of the pigment itself, does not remove it from the prepared and pure turacin, it is evident that this metal, copper, is an integral constituent of the substance under investigation. Some idea may be formed of the intimate union subsisting between the copper and the other constituent elements of the colouring-matter, from the observation that turacin, dissolved in oil of vitriol and reprecipitated by excess of sodium acetate, suffers by this treatment no loss of copper.

The different parts of eighty-seven red feathers of *Corythæix albocristata* have been carefully examined. From the red barbs of these a considerable quantity of turacin was prepared, while their shafts were submitted to special dissection. The clear horny parts, or quills proper, at the base of each feather were cut off and separately incinerated; so also were the upper parts or shafts of the eighty-seven feathers, and, in like manner, the membranes found in the quills. There was no copper in the ash of the eighty-seven quills, and none in that of the membranes; but a very minute trace was recognized in the ash of the shafts.

There is therefore no possibility of any mistake having occurred as to the copper present in the red parts of the feathers of the Touracous. It cannot have been introduced in any preservative solution, for it would then be found in the black parts of the

web as well as in the red; it cannot be an artificial dye, for birds bred in captivity acquire the cupreous pigment naturally*; it cannot be an accidental and unnecessary constituent of the red colouring-matter; for not only is it impossible to remove this metal from the pigment, but the proportion of copper present in the turacin obtained from different species of Plantain-eaters remains constant. I will now state what this proportion is.

In my earliest analysis of turacin I employed a specimen which had been precipitated by acetic acid from the alkaline extract of the feathers. Now, on burning some turacin thus prepared, I found that it left a very considerable amount of ash, nearly twice as much as in subsequent experiments where hydrochloric acid had been used as the precipitant of the pigment. Some calcium, magnesium, and ferric phosphates had obstinately adhered to the precipitated turacin, and increased to a marked extent its normal quantity of ash. The same salts accompany the colouring-matter of blood with similar tenacity. But it was soon found that the new pigment might be obtained in such a state of purity as to leave no other ash when burnt than nearly pure cupric oxide, the 7 per cent. of phosphates &c. having been previously removed by the action of hydrochloric acid without any change in the turacin itself. In the analyses which follow, turacin precipitated by hydrochloric acid was employed; the amount of ash other than cupric oxide will be seen to amount to about 1 per cent. only of the substance analyzed. I may add that even this residual impurity may be completely removed by the further employment of hydrochloric acid.

Analysis.	Turacin taken.	Total ash.	Ash per cent.	
i.	·1293 grm.	·0108	8·35	
ii.	·0558	·0048	8·60	
	Turacin taken, corrected for ash.	CuO obtained.	CuO per cent.	Cu per cent.
iii.	·125	·0090	7·20	5·75
iv.	·061	·0045	7·38	5·89
v.	·053	·0040	7·55	6·03
vi.	·1553	·0115	7·41	5·91

Some difficulty was experienced in determining the nitrogen contained in turacin. The first combustions were made with soda-lime; but attempts to obtain, with the ammonia evolved, a satisfactory platinum-salt were unsuccessful. The NH_3 is accompanied by a substance which reduces the platinic chloride. More satisfactory and accordant results were secured when the ammonia evolved by turacin on combustion with soda-lime was received into standard sulphuric acid, and the amount of this acid thereby neutralized ascertained by a standard soda-solution. Finally, however, a modification of DUMAS'S absolute method of determining nitrogen as gas was adopted: the method was as follows.

The substance, dried at 100° , was burnt with cupric oxide in a combustion-tube 2 feet in length, in which was contained, at its remote end, 6·5 grms. of pure sodium bicarbonate. Next to this was a layer of cupric oxide, then the mixture of turacin and

* Private contribution from J. J. MONTEIRO, Esq., Dec. 10, 1867.

cupric oxide. The rest of the tube was occupied by cupric oxide and 6 inches of clean reduced copper turnings. After clearing the apparatus of air by decomposing part of the sodium bicarbonate, the combination was commenced, the gases being delivered into a eudiometer standing over mercury, and partly occupied with a layer of caustic potash solution. The combustion finished, the tube was swept out by decomposing the remainder of the bicarbonate. The eudiometer and its contents were transferred to a vessel of water, and the pure nitrogen gas it contained read off with the customary precautions.

The following results were obtained in three analyses:—

Analysis	vii.	viii.	ix.
Observed volume	47.6 millims.	53.8 millims.	50.2 millims.
Volume corrected for calibre and meniscus	47.14 millims.	53.51 millims.	49.8 millims.
Temperature of gas	7° 0 C.	8° 1 C.	13° 0 C.
Barometer	739.0 millims.	733.75 millims.	753.6 millims.
Temperature of barometer	13° 3 C.	16° 1 C.	15° 0 C.
Water-column	497.9 millims.	495.2 millims.	495.3 millims.

The observed volume of nitrogen was also corrected for the tension of aqueous vapour, and the barometric reading for expansion of the brass scale. The usual formula of calculation was adopted,

$$v' = \frac{v \left(b - \frac{b_1}{13.596} - b_2 \right)}{760(1 + .00366 t^\circ)},$$

where

v represents the observed volume corrected for calibre and meniscus.

b the height of the barometer corrected for expansion.

b_1 the water-column in the eudiometer.

b_2 the tension of aqueous vapour at t° C., in millims.

t° the temperature of gas.

v' the true volume of gas in millims. (1 millim. = .1786 cub. centim.)

The following are the final results of the three nitrogen-determinations, vii., viii., ix.:—

	vii.	viii.	ix.
Turacin taken1445	.1665	.1604
Turacin, corrected for ash1431	.1648	.1588
Volume of nitrogen in cub. centims. at 0° C. and 760 millims. bar.	7.485	8.385	7.864
Weight of this nitrogen00939	.01052	.009866
Percentage of nitrogen	6.56	6.38	6.21

The determinations of carbon and hydrogen in turacin were made by burning the substance with cupric oxide containing some lead chromate, reduced copper turnings being placed in the anterior part of the tube. Every precaution was taken in these combus-

tions to ensure trustworthy results, especially as, on account of its rarity and costliness, the amount of material burnt was necessarily small.

Analysis	x.	xi.	xii.	xiii.
Turacin taken	·1040	·1400	·0835	·1937
Turacin, corrected for ash .	·1030	·1385	·0825	·1916
CO ₂ obtained	·2065	·2780	·1635	·3828
H ₂ O obtained	—	·0670	·0390	·0870
Percentage of carbon . .	54·66	54·75	54·06	54·49
Percentage of hydrogen .	—	5·38	5·21	5·06

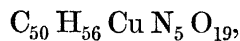
I have gathered into the following Table the percentage results deduced from the analyses above given:—

Carbon.	Hydrogen.	Copper.	Nitrogen.
54·66	5·75	6·56
54·75	5·38	5·89	6·38
54·06	5·21	6·03	6·21
54·49	5·06	5·91	
54·49	5·22	5·90	6·38

If, however, we exclude the low percentage of carbon (54·06) obtained in one case where the amount of substance taken was insufficient to secure an accurate result, we may deduce the following mean percentages as representing the centesimal composition of turacin dried at 100° C.:—

Carbon	54·63
Hydrogen	5·22
Copper	5·90
Nitrogen	6·38
Oxygen (diff.)	27·87
	<hr/> 100·00

If we assume that one molecule of turacin contains one atom of copper, we are led to conclude that the relations between its constituents may possibly be represented by the empirical formula



which demands the following percentages:—

	Theory.	Experiment. (Mean.)
C ₅₀ = 600·0	54·87	54·63
H ₅₆ = 56·0	5·12	5·22
Cu = 63·5	5·81	5·90
N ₅ = 70·0	6·39	6·38
O ₁₉ = 304·0	27·81	27·87
	<hr/> 1093·5	<hr/> 100·00
	100·00	100·00

I do not wish to attach great importance to the above formula for turacin; but it certainly represents the analytical results closely, and possesses, in its atom of copper, an element of control similar to that of a metallic salt. In its permanence and its constancy of composition, turacin is separated widely from complex bodies like the albuminoids, which in many particulars it resembles; for it must be here noted that the analyses above given have been made with different specimens of turacin—some with specimens from *Musophaga violacea*, but in most instances with the pigment from the *Corythaix albocristata*, or *C. porphyreolopha*. Notwithstanding this diversity of origin, and certain changes in the modes of preparation, the analytical results have been remarkably concordant.

Affinities of Turacin.—In its colour, in its absorption-spectrum, and in some of its other characters, turacin corresponds closely with the scarlet cruorin of blood, yet it contains no iron, or, at most, an inappreciable trace of this metal. Iron, however, exists to the extent of between 6 and 7 per cent. in hæmatin, the chief derived colouring-matter obtained from blood, and is doubtless a constituent of the original cruorin; yet if, in turacin, the iron of cruorin is replaced by copper, there are other and wider differences of composition and deportment between the two pigments, which prevent us from regarding turacin as a *copper cruorin*. Moreover turacin does not seem to occur in corpuscles, but to be homogeneously distributed in the barbs, barbules, and crochets of the red feathers in which it occurs.

Turacin seems to characterize the closely allied genera *Musophaga* and *Corythaix*. These birds, though with the other Touracous distinctive of the African Ornis, are not common; and in consequence the supply of turacin for experimental purposes is very limited. I have not detected it in any of the other red-plumaged birds which I have examined. The quantity of turacin in a single bird is small. It is most abundant at the pairing-season, and the bridal plumage of a *Corythaix albocristata* generally yields from two to three grains of the pigment. One bird, then, may contain in the colouring-matter of its wings nearly .2 of a grain of metallic copper.

Turacin is the first animal or vegetable pigment containing copper as an essential constituent which has hitherto been isolated; yet traces of copper have been repeatedly found in both animals and plants. It was detected by HARLEN in the blood of certain Ascidia and Cephalopoda. It occurs in *Limulus cyclops*, *Cancer pagurus*, *Acanthias zeus*, and *Conger vulgaris*, its quantity being in inverse ratio to the quantity of iron present. The blood of *Helix pomatia* contains much copper, the part of the ash insoluble in water yielding 2.57 per cent. Many chemists have detected minute traces of copper in human blood; and twenty years ago DESCHAMPS arrived at the conclusion that it is normally contained in the blood of man and animals. ODLING and DUPRÉ have indeed subsequently detected copper in flour, straw, hay, meat, eggs, cheese, and other articles of food. It has been supposed that the copper detected in some of these substances has been introduced in the course of analysis by the use of brass burners and retort rings; but these in most cases are a purely imaginary source of error. It is not

difficult to perceive whence the Touracous derive the copper which their red feathers contain; and I have actually succeeded in obtaining unmistakable indications of copper from the ash of three fruits of a plantain, the common *Musa sapientum*. There is, of course, still room for experiment and further observation in this direction. Researches as to the source of copper whence vegetables assimilate it, the occurrence of ores of copper near the habitats of the Touracous, and its detection in the articles of food supplied to these birds when kept in captivity will doubtless lead to interesting results. The whole subject of the occurrence of copper in animal products is fraught with physiological as well as chemical interest.

In conclusion I must express my obligation for the assistance afforded me, during the progress of the present inquiry, by those friends whose names I have already mentioned, and by others who have rendered me special aid. To Dr. J. H. GLADSTONE I am indebted for the drawings of spectra which accompany this paper; to PHILIP COURT, Esq., of Port Elizabeth, for an ample supply of Touracous when the stores of the London natural-history dealers were exhausted; and, especially, to my assistant, Mr. B. J. GROSJEAN, for the laborious and conscientious care with which he has executed nearly the whole of the analytical work involved in the present research.